Assessment of Adsorption Potential of Activated Carbon from Marula De-Oiled Seed Cake Prepared by Chemical Activation with Potassium Hydroxide

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Abstract- Activated carbon is a very important porous substance that is employed in various industrial applications. In this study, AC was synthesized from marula seed cake via singled-step activation with KOH and then thermally treated at 400, 500 and 600oC for an hour. The results indicates that increasing the activation temperature causes increased in rate of carbon adsorption. However, it was found that the activated carbons were within the microporous range with highest specific surface area of 368.396 m2/g at activation temperature of 600°C.

Indexed Terms- Marula de-oiled seed cake, Activated carbon, Singled-step activation, Microporous

I. INTRODUCTION

The use of lignocellulosic biomass to create activated carbon is a significant method for addressing air pollution. This type of biomass consists largely of agricultural waste, which is plentiful. Transforming these wastes into valuable products like activated carbon can help alleviate environmental issues, including the buildup of agricultural waste, air pollution, and water contamination. Additionally, utilizing activated carbon derived from lignocellulosic biomass instead of fossil fuels, such as coal, can mitigate the impacts of global warming. Thus, the exchange of carbon between the atmosphere and the pollutant removal processes constitutes a carbon-neutral cycle. Besides being efficient at removing pollutants, activated carbon from lignocellulosic sources is cost-effective due to its abundance in agricultural waste (Nor et al., 2013).

Activated carbon (AC) features a well-defined pore structure, high surface area, amphoteric properties conducive to electron transfer, and significant adsorptive capacity (Cazetta et al., 2011). Its chemical properties are largely determined by the surface group composition and the chemical bonding of heteroatoms (Ukanwa et al., 2019). The characteristics of activated carbon are influenced by the physical and chemical properties of the raw materials and the activation process used (Verla et al., 2012). Functional groups play a crucial role in defining key attributes of activated carbon, including acidity, hydrophobicity, polarization intensity, and adsorption capabilities (Sugumaran et al., 2012).

Activated carbon is extensively employed in wastewater treatment to eliminate toxic chemicals and heavy metals from industrial effluents or flue gas (Amuda and Ibrahim, 2006). Its applications in industry range from removing organic and inorganic contaminants from drinking water to treating industrial wastewater, decolorizing syrups, and purifying air and pharmaceuticals (Chipofya and McConnachie, 2000). With the growing industrial demand for activated carbon, which is often quite costly, there is a push to explore cheaper alternatives derived from agricultural waste or residues, such as seed cakes, rice husk, sawdust, and other carbon-rich materials. Therefore, assessing other available biomass sources is very essential.

The present study investigates the use of de-oiled marula seed cake as a raw material in the production of carbon adsorbents through singled step activation with KOH. The influence of the activation temperature on the adsorption capacity of the adsorbent was investigated.

II. MATERIALS AND METHODS

Preparation of the Activated Carbons

De-oiled marula seeds cake (100 g) was transferred into beakers (250 cm^3). To it, was added distilled water heated at 80°C and the content allowed to stand for hours, and the supernatant decanted to remove traces of oil/dirt. After washing with distilled water, the biomass was dried in oven at 105°C overnight. The dried seeds cake was then powdered and impregnated with KOH (1.0M). The impregnated biomass was stirred over magnetic stirrer for 2 h at ambient temperature. The dried impregnated sample was carbonized in a muffle furnace at different temperature (400, 500 and 600°C) for an hour. The resulting activated carbon was washed with 0.5 M HCl followed by distilled water.

Determination of Ammonia Adsorption

A constant amount (1.0g) of the activated carbon samples was used to determined adsorption potential of the synthesized carbons with ammonia solution in accordance with method reported by Njewa et al, (2022). The adsorption percentage was calculated using the equation reported by (Ahnemark and Marques, 2013).)

$$\text{Adsorption (\%)} = \frac{\Delta m}{M_b} \text{ x } 100$$

where Δm is the change in mass of activated carbon after ammonia adsorption and M_b is the original mass of the activated carbon before adsorption.

Characterization of the Seeds Cake and the Carbon

Proximate analyses of dried marula seed cake (MSC) powder and the produced activated carbon were conducted in accordance with ASTM E 870-82, while ultimate analyses were performed following ASTM D3176-89 guidelines. The surface functional groups of both the marula seed cake and the synthesized activated carbon were examined using Fourier transform infrared (FTIR) spectroscopy (FTIR-is50ABx). The surface morphology of the materials was observed with a scanning electron microscope (SEM inspect F50 USA). The X-ray diffraction of the activated carbons (MSC-AC) was assessed using an X-ray diffractometer (XRD-7000). Additionally, the BET surface area, micropore volume, and micropore surface area of the activated carbons were determined using the Brunauer-Emmett-Teller (BET) method.

III. RESULTS AND DISCUSSION

Pore-size distribution of the synthesised carbons

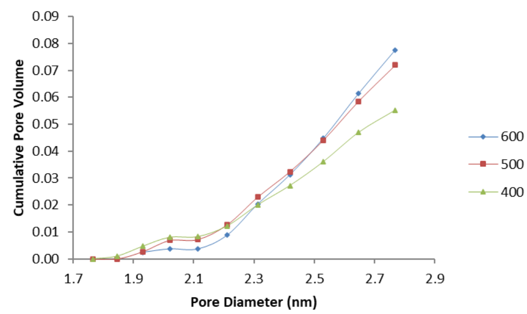

Figure 1: The effect of activation temperatures on pore size distribution

Pore-size distribution is a vital characteristic of activated carbons (ACs) as it influences their adsorption performance as adsorbents and the effectiveness of ionic transport in supercapacitors across various industrial applications. Effective matching between ions and pores enhances the utilization of pores, promoting the development of the double layer structure, which improves capacitance. To adequately accommodate electrolyte ions in microporous or mesoporous carbon materials, it is essential to refine pore size accurately (Herde et al., 2020). Figure 1 illustrates the pore size distribution of ACs, revealing that those prepared at temperatures of 400, 500, and 600 °C have pores ranging from 1.76 to 2.76 nm. A notable amount of the activated pores falls within the microporous range (1 – 2 nm) along with narrow mesopores (2 – 6 nm). As noted by Fu et al. (2020) and Mistar et al. (2020), the pore structure of ACs primarily forms through the release of volatile content, gasification, and reactions involving carbonates and/or oxides from KOH interacting with carbon atoms. The pore size distribution of these activated carbons indicates the presence of both micropores and mesopores. Higher activation temperatures result in an increase in pore volume, and any changes in the particle size distribution shape with rising activation temperature reflect alterations in the pore structure (Agboola et al., 2018).

The influence of Temperature on the Surface area and Microvolume

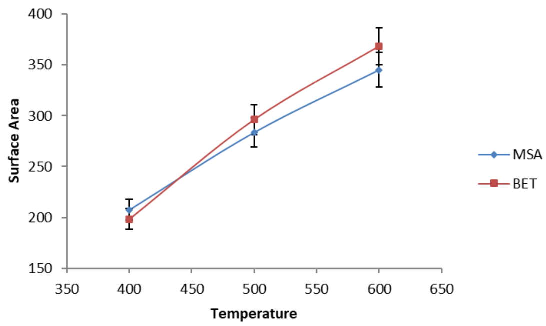

Figure 2: The influence of activation temperature on the Surface area

As shown in Fig. 2, both the BET and micropore surface areas rise as the activation temperature increases from 400 °C to 800 °C. During the chemical activation of the sample with KOH, a transition from microporosity to mesoporosity was noted (Fig. 2). This may be attributed to the release of tar during the intense activation of the activated carbon, leading to an expansion of porosity within the activated carbon layer. Nonetheless, the uneven distribution of KOH throughout the powdered sample might lead to hyperactivation after heating, which could collapse pore walls and expand micropores into mesopores (El-Nemr et al., 2022). The specific surface area of the activated carbon increased from 198.46 to 368.39 m2/g as the activation temperature rose from 400 °C to 800 °C. The findings also indicated that the micropore volume increased from 0.179 to 0.307 cc/g with the temperature increase.

Table 1: Textural parameters of the carbon at different activation temperature

Temperature	BET (m^2/g)	MSA (m^2/g)	V_{mic} (cc/g)	Pore diameter (nm)
400	198.468	207.503	0.179	2.446
500	296.273	283.728	0.258	2.116
600	368.396	345.184	0.307	2.137

Table 2: Comparison of Surface Area of activated carbon from Marula De-oiled seeds cake with other literatures

Substrates	Time (min)	Conc. KOH	Temp (°C)	S_{BET} (m^2/g)	Reference
Rice husk	120	1 M	800	1836	Shen and Fu (2018).
Casuarina fruit waste	60	10 %	600	218	Ravichandran et al., (2018)
Mombin fruit	60	-	500	167	Junqueira et al., (2018)
Rubber seed shell	120	Overnight	700	1129	Borhan et al., (2019)
karanja oil seed cake	120	-	500	343	Ganvir et al., (2012)
Marula de-oiled seed cake	60	1 M	600	368.39	This study

In single-step chemical activation, impregnation is typically performed prior to carbonization. This activation process hinges on several critical factors, including the concentration of the chemical agent, the impregnation ratio, and the temperature and duration of carbonization, all of which are essential for achieving optimal activated carbon properties. However, an excessive concentration of KOH can lead to over-activation, resulting in the destruction of the microporous structure of the carbon and the formation of larger pores (Yang et al., 2017). The same principle applies to the impregnation ratio as well. Table 2 illustrates various studies on activated carbon derived from different biomass sources through single-step KOH activation. The concentration of the activator and the carbonization temperature significantly influence the surface area and pore structure of the activated carbon.

Adsorption Potential of the Synthesized Carbons

Figure 3 illustrates the ammonia adsorption rates on activated carbons at temperatures of 400, 500, and 600 °C. The findings demonstrate that as the carbonization temperature rises from 400 °C to 600 °C, the adsorption rates increase correspondingly. This effect can be linked to the heat treatment process, which enhances the opening and widening of pores, thereby enlarging the surface area. However, excessive heat treatment may lead to the burning off of carbon, which can negatively impact pore size and surface area, subsequently influencing the adsorption capacities (Muniandy et al., 2014 and Bernardo et al., 2016). The highest ammonia adsorption percentage of 56.25% was recorded at an activation temperature of 600 °C.

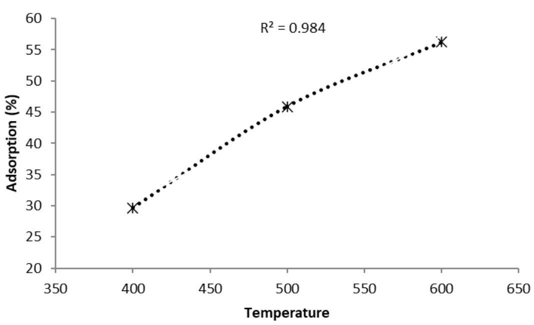

Figure 3: Adsorption percentage of the prepared activated carbon

CONCLUSION

The study has shown that the prepared activated carbons were microporous, with a very good surface area of 368.396 m^2/g. The study, however, demonstrated that the marula seeds cake could be a potential raw materials to prepare low-cost and high-porous carbon addorbent for chemical pollutants. In terms of misoporosity and specific surface area, ammonia adsorption reached a maximum value (56.25 %) at the highest activation temperature.

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